Overview of ALD Precursors and Reaction Mechanisms

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Abstract

Successful use of ALD requires suitable chemical precursors used under reaction conditions that are appropriate for them. There are many requirements for ALD precursors: sufficient volatility, thermal stability and reactivity with substrates and with the films being deposited. In addition, it is easier to produce the required vapors if the precursor is liquid at room temperature, or if it is a solid with melting point below the vaporization temperature, or if it is soluble in an inert solvent with vapor pressure similar to that of the precursor. The precursor vapor should not etch or corrode the substrate or deposited film. Ideally, the precursors should be non-flammable, non-corrosive, non-toxic, simple and non-hazardous to make and inexpensive.

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Introduction to
ALD Precursors and Reaction Mechanisms

Tutorial for ALD 2011

Roy Gordon
Harvard University

Outline

- Elements and Materials in ALD Films
- ALD Precursors for Non-Metals
- Types of ALD precursors for Metals
- Types of ALD Reactions

ELEMENTS AND MATERIALS IN ALD FILMS

List of the Stable Elements by Symbol

Silver	Ag	Europium	Eu	Manganese	Mn	Antimony	Sb
Aluminum	Al	Fluorine	F	Molybdenum	Mo	Scandium	Sc
Argon	Ar	Iron	Fe	Nitrogen	N	Selenium	Se
Arsenic	As	Gallium	Ga	Sodium	Na	Silicon	Si
Gold	Au	Gadolinium	Gd	Niobium	Nb	Samarium	Sm
Boron	B	Germanium	Ge	Neodymium	Nd	Tin	Sn
Barium	Ba	Hydrogen	H	Neon	Ne	Strontium	Sr
Beryllium	Be	Helium	He	Nickel	Ni	Tantalum	Ta
Bromine	Br	Hafnium	Hf	Oxygen	O	Terbium	Tb
Carbon	C	Mercury	Hg	Osmium	Os	Tellurium	Te
Calcium	Ca	Holmium	Ho	Phosphorus	P	Thallium	Tl
Cadmium	Cd	Iodine	I	Lead	Pb	Thulium	Tm
Cerium	Ce	Indium	In	Palladium	Pd	Titanium	Ti
Chlorine	Cl	Iridium	Ir	Praseodymium	Pr	Tungsten	W
Cobalt	Co	Potassium	K	Platinum	Pt	Vanadium	V
Chromium	Cr	Krypton	Kr	Rubidium	Rb	Xenon	Xe
Cesium	Cs	Lanthanum	La	Rhenium	Re	Yttrium	Y
Copper	Cu	Lithium	Li	Rhodium	Rh	Ytterbium	Yb
Dysprosium	Dy	Lutetium	Lu	Ruthenium	Ru	Zinc	Zn
Erbium	Er	Magnesium	Mg	Sulfur	S	Zirconium	Zr

Periodic Table

metals

metalloids or semi-metals

non-metals

main group metals

alkali metals

alkaline earth metals

transition metals

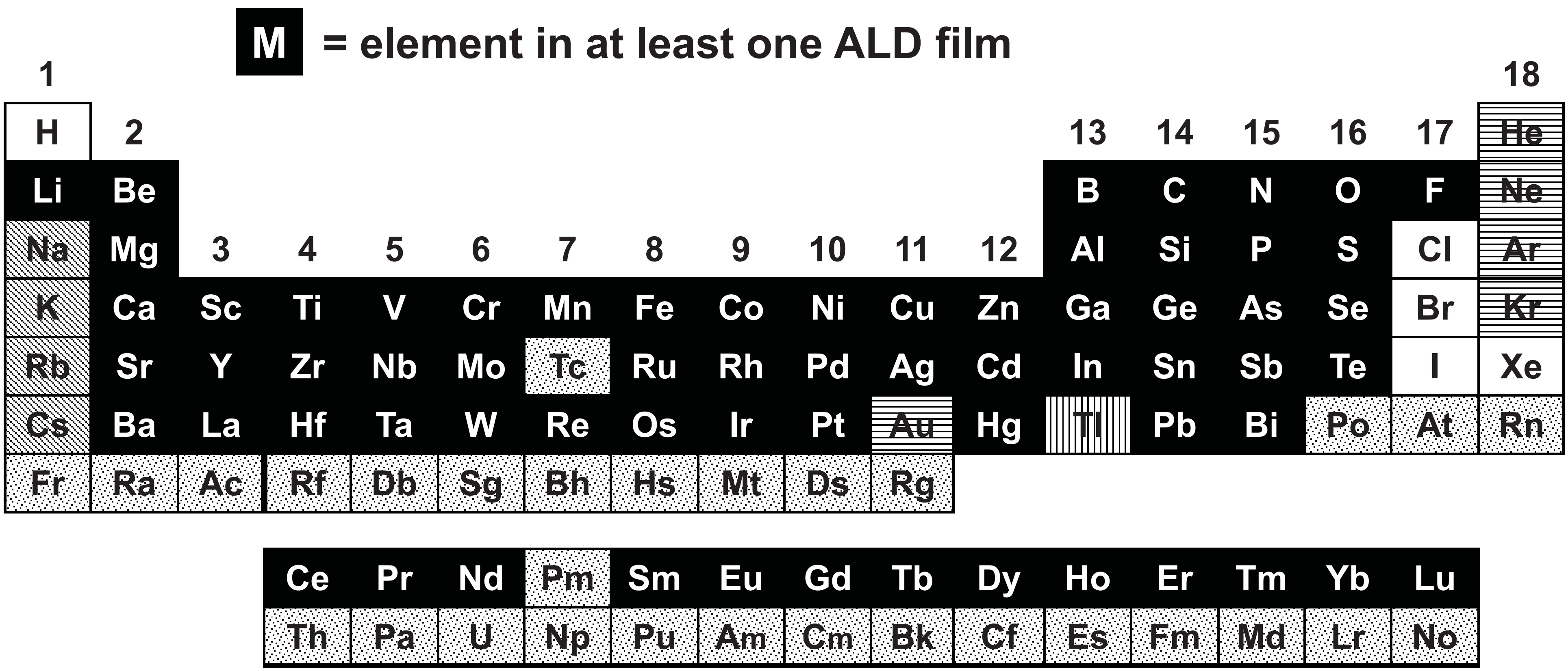
halogens

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

main group metals

lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Elements in ALD Films



Not used in ALD because the elements are

= low-volatility compounds = radioactive = highly toxic = inert

Combinations of Elements in ALD Films

ALD films have been made with combinations of 2 or more elements within a box

Underlined elements have been deposited as pure, single elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
O Li	O Be											N O P B	C	N
Na	O F Mg Te											N O P Al As	N O P Si C	B O Si P
K	O F Ca S	N O Sc	N O Zr Ti S Hf Al C	O V	O Cr Al	N O Mn S Te	N O Fe	N O Co	N O C Ni S	N O Cu S	N O F Zn S Te Se	N O P Ga As	O Ge Sb Te	As
Rb	O F Sr S Ti	N O Y S	N O Si Zr Ti Al	N O Nb	N Mo	Tc	O Ru	O Rh	Pd	Ag	Cd S Te Se	N O P In S As Sb	O Sn S	O Sb Te
Cs	O Ba S Ti	N O F Si La S Al	N O Si Hf Ti Al	N O Ta C	N O W S Si C	Re	Os	O Ir	Pt	Au	Hg Te	Tl	O Pb S Ti	O Si Bi Ti
	O Ce	O Pr	O Nd	Pm	O Sm	O Eu	O Gd	O Tb	O Dy	O Ho	O Er	O Tm	O Yb	N O Lu

Updated table from R. Puurunen, *J. Appl. Phys.* 97, 121301 (2005)

ALD Materials by Type

Oxide dielectrics	Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Sc_2O_3, Y_2O_3, MgO, B_2O_3, SiO_2, GeO_2, La_2O_3, CeO_2, PrO_x, Nd_2O_3, Sm_2O_3, EuO_x, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, Bi_xTi_yO, Bi_xSi_yO, $SrTa_2O_6$, $SrBi_2Ta_2O_9$, $YScO_3$, $LaAlO_3$, $NdAlO_3$, $GdScO_3$, $LaScO_3$, $LaLuO_3$, $LaYbO_3$, $Er_3Ga_5O_{13}$
Oxide conductors or semiconductors	In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, Sb_2O_3, ZnO, ZnO:Al, ZnO:B, ZnO:Ga, RuO_2, RhO_2, IrO_2, Ga_2O_3, VO_2, V_2O_5, WO_3, W_2O_3, NiO, CuO_x, FeO_x, CrO_x, CoO_x, MnO_x
Other ternary oxides	$LaCoO_3$, $LaNiO_3$, $LaMnO_3$, $La_{1-x}Ca_xMnO_3$
Nitride dielectrics or semiconductors	BN, AlN, GaN, InN, Si_3N_4, Ta_3N_5, Cu_3N, Zr_3N_4, Hf_3N_4, LaN, LuN
Metallic nitrides	TiN, Ti-Si-N, Ti-Al-N, TaN, NbN, MoN, WN_x, WN_xC_y, Co_xN, Sn_xN
II-VI semiconductors	ZnS, ZnSe, ZnTe, CaS, SrS, BaS, CdS, CdTe, MnTe, HgTe
II-VI based phosphors	ZnS:M (M=Mn,Tb,Tm); CaS:M (M=Eu, Ce, Tb, Pb); SrS:M(M=Ce,Tb, Pb)
III-V semiconductors	GaAs, AlAs, AlP, InP, GaP, InAs
Fluorides	CaF_2, SrF_2, MgF_2, LaF_3, ZnF_2
Elements	Ru, Pt, Ir, Pd, Rh, Ag, Cu, Ni, Co, Fe, Mn, Ta, W, Mo, Ti, Al, Si, Ge
Other semiconductors	PbS, SnS, In_2S_3, Sb_2S_3, Cu_xS, $CuGaS_2$, WS_2, SiC, $Ge_2Sb_2Te_5$
Others	La_2S_3, Y_2O_2S, TiC_x, TiS_2, TaC_x, WC_x, $Ca_3(PO_4)_2$, $CaCO_3$, organics

Adapted from M. Ritala and J. Niinisto, in *Chemical Vapor Deposition* (Royal Society of Chemistry, 2009)

ALD PRECURSORS FOR NON-METALS

oxygen

nitrogen

fluorine, carbon

sulfur, selenium, tellurium

phosphorus, arsenic, antimony

Non-Metals Important in ALD Films

C = Carbon **N = Nitrogen** **O = Oxygen** **F = Fluorine**

P = Phosphorus **S = Sulfur**

Se = Selenium

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No	

ALD Precursors for Oxygen

Water vapor, H_2O

Hydrogen peroxide, H_2O_2, sometimes more reactive than H_2O (always accompanied by water)

Alcohols, ROH, such as methanol CH_3OH or ethanol C_2H_5OH

Di-oxygen, O_2, the common form of oxygen in the air

Ozone, O_3, a more reactive form of oxygen, made in a plasma, can flow through tubing; (always accompanied by O_2)

Oxygen atoms, created in a plasma close to a substrate surface; so reactive that they can’t travel far through tubing without recombining to form O_2

Nitrogen dioxide, NO_2 (always accompanied by its dimer N_2O_4)

ALD Precursors for Nitrogen

Ammonia, NH_3

Hydrazine, N_2H_4, is more reactive than NH_3, but toxic & explosive

Plasma-activated NH_3 is more reactive than NH_3

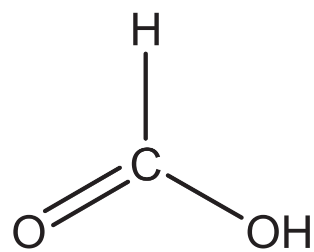
Dinitrogen, N_2, is normally unreactive under ALD conditions

Plasma-activated N_2 is more reactive than N_2

Nitric oxide, NO, can be used for nitrogen-doping of oxides

ALD Precursors for Carbon

Acetylene gas 

Formic acid vapor 

Carbon contained in a metal compound

ALD Precursors for Fluorine

Hydrogen fluoride gas, HF

Fluorine contained in a metal compound such as WF_6

ALD Precursors for Sulfur, Selenium and Tellurium

Elemental sulfur vapor, S_n

Hydrogen sulfide gas, H_2S (poisonous, but sufficient warning by smell, if not chronically exposed)

Hydrogen selenide gas, H_2Se (very poisonous, without sufficient warning by smell)

Bis(triethylsilyl)selenium, $(Et_3Si)_2Se$

Bis(triethylsilyl)tellurium, $(Et_3Si)_2Te$

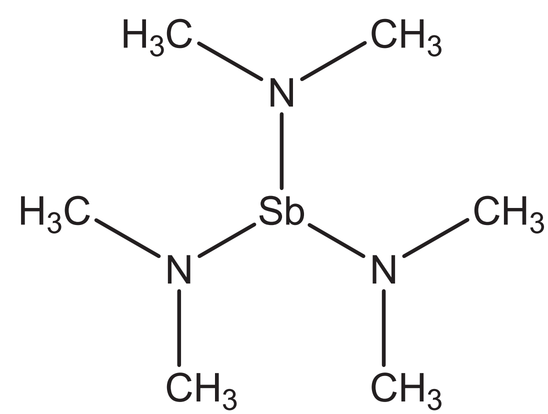
ALD Precursors for Phosphorus, Arsenic and Antimony

phosphine gas, PH_3 (very poisonous)

arsine gas, AsH_3 (very poisonous)

antimony trichloride, $SbCl_3$

tris(dimethylamido)antimony



Elemental ALD Precursors

Examples:
Non-metals O_2, P_4, S_2 or S_8
Metals: Mg, Mn, Zn

Advantage: high purity

Disadvantage: low volatility (metals)

1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

TYPES OF ALD PRECURSORS FOR METALS

pure elements

metal hydrides

metal halides: fluorides, chlorides, bromides, iodides

metal-carbon bonds: alkyls, cyclopentadienyls

metal-oxygen bonds: alkoxides, beta-diketonates

metal-nitrogen bonds: amides, imides, amidinates

Metal Compounds for ALD

Most metal compounds used in ALD have 1 or 2 metal atoms, M, combined with 1 or more "ligands", L, written as monomers ML_n or dimers M_2L_n, where n = 1, 2, 3, 4, 5 or 6.

The ligands, L, contain 1 or more non-metal atoms.

The metal atoms, M, may be considered to have $\geq$1 units of positive charge.

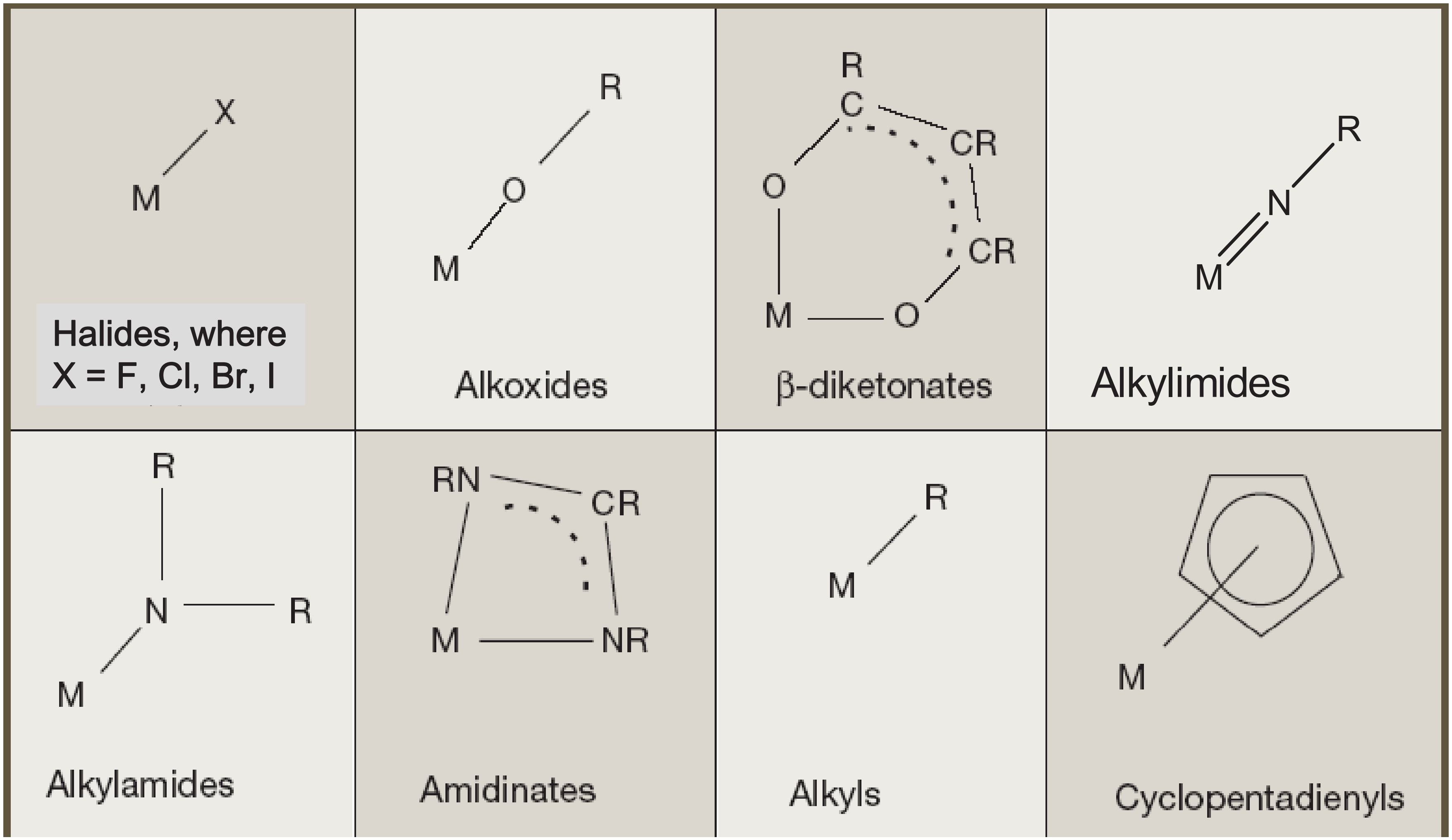
Metals with 1 unit of positive charge M^+ may be written M(I), and are said to be in oxidation state +1.

Metals with 2 units of positive charge M^{2+} may be written M(II), and are said to be in oxidation state +2, etc.

Most ligands used in ALD can be considered to have electrical charge -1. A few ligands, e.g. oxides (O^{2-}) and imides $(NC_xH_{2x+1})^{2-}$, have charge -2.

The total charges of the metal and ligands in a precursor must add to zero.

Types of Metal Precursors for ALD



R = alkyl group = C_nH_{2n+1}

Elements with Hydride ALD Precursors

Hydrides are compounds of an element X and hydrogen

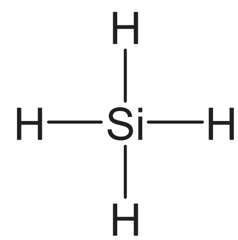
XH_n n = 1, 2, 3 or 4

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

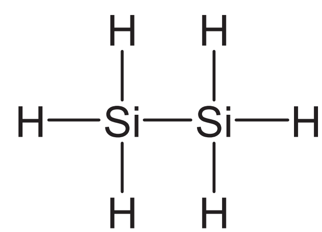
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Examples of Hydride Precursors

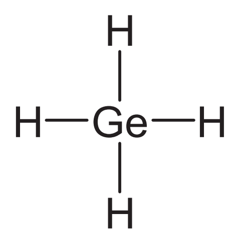
SiH_4 = silane



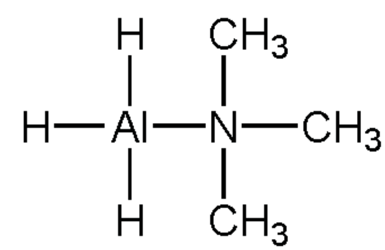
Si_2H_6 = disilane,
more reactive than silane



GeH_4 = germane



AlH_3 NMe_3 = aluminum hydride – trimethylamine



Advantage:
very volatile

Disadvantages:
usually need plasma activation
pyrophoric and toxic

Elements with Halide ALD Precursors

Halides are compounds of an element M and a halogen X = F, Cl, Br or I

MX_n n = 1, 2, 3, 4, 5 or 6

halogens

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Examples of Halide ALD Precursors

WF_6 = tungsten hexafluoride

$TiCl_4$ = titanium tetrachloride

$HfCl_4$ = hafnium tetrachloride

$SnCl_4$ = tin tetrachloride

Advantages:
thermally stable
usually inexpensive

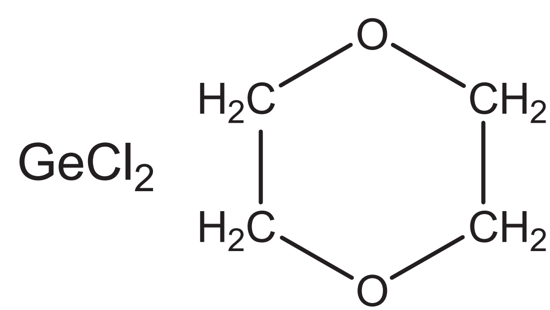
Disadvantages:
halogen impurities in films
corrosive byproducts
low volatility for some elements

Oxygen can be combined with halide ligands:

$VOCl_3$ = trichlorooxovanadium
= vanadium oxide trichloride
= vanadyl trichloride

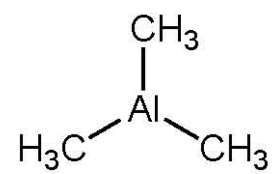
CrO_2Cl_2 = dichlorodioxochromium
= chromium dichloride dioxide
= chromyl dichloride

$GeCl_2 \cdot$dioxane

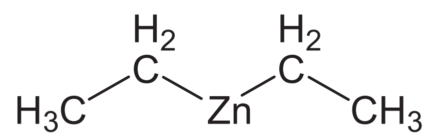


Metal Alkyl ALD Precursors

$(CH_3)_3Al$ = trimethylaluminum



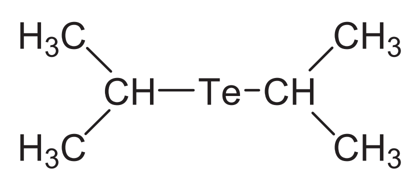
$(CH_3CH_2)_2Zn$ = diethylzinc



Advantage: volatile, highly reactive in ALD

Disadvantage: hazardous, burst into flame in air (pyrophoric)

$^iPr_2Te$ = diisopropyltellurium

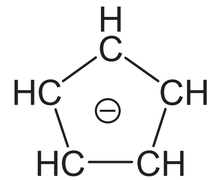


Elements with Alkyl ALD Precursors

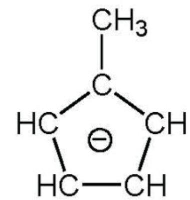
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											**B**	C	N	O	F	Ne
Na	Mg											**Al**	**Si**	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	**Zn**	**Ga**	**Ge**	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	**Hg**	Tl	Pb	**Bi**	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No	

Cyclopentadienyl Ligands

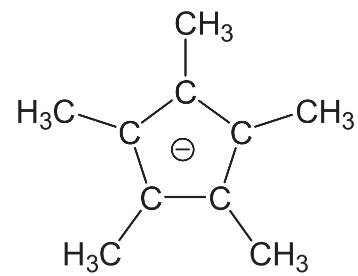
Cp = cyclopentadienyl



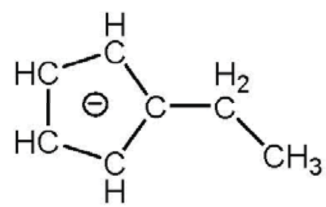
MeCp = methylcyclopentadienyl



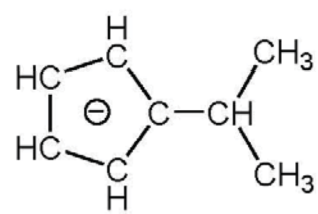
Me_5Cp = Cp* = pentamethylcyclopentadienyl



EtCp = ethylcyclopentadienyl



$^{i}PrCp$ = isopropylcyclopentadienyl



Examples of Cyclopentadienyl Precursors

Cp_2Ni = bis(cyclopentadienyl)nickel(II)

$(EtCp)_2Ru$ = bis(ethylcyclopentadienyl)ruthenium(II)

$(Me_5Cp)_2Sr$ = bis(pentamethylcyclopentadienyl)strontium

$(^iPrCp)_3La$ = tris(isopropylcyclopentadienyl)lanthanum

Cp_2Me_2Zr = (dicyclopentadienyl)(dimethyl)zirconium

$(MeCp)(Me)_3Pt$ = (methylcyclopentadienyl)(trimethyl)platinum(IV)

Cyclopentadienyl ALD Precursors

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

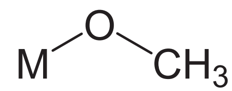
Advantages:

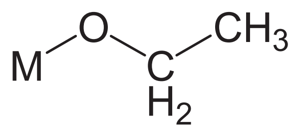
thermally stable

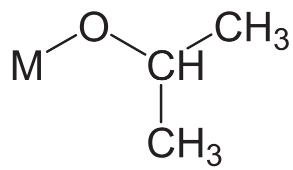
Disadvantages:

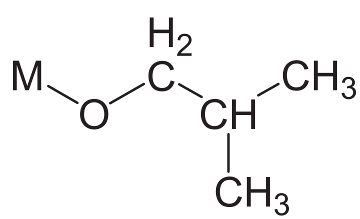
some have low reactivity (Ni, Ru)
some are solids (Ni, Sr, Mg, In, La)
some have low volatility (La, Sr, Mg)

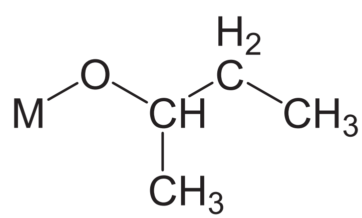
Alkoxide Compounds

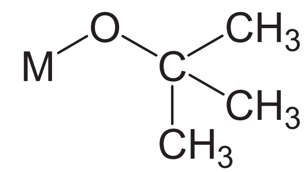
OMe = methoxy 

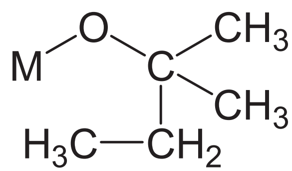
OEt = ethoxy 

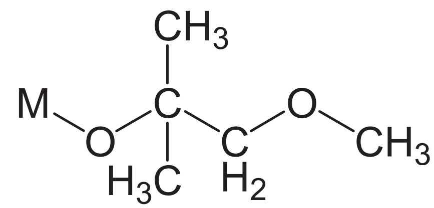
O^iPr = isopropoxy 

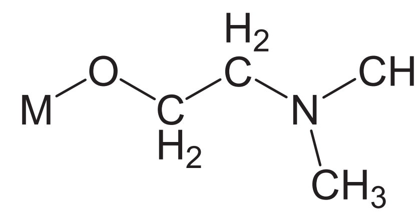
O^iBu = isobutoxy 

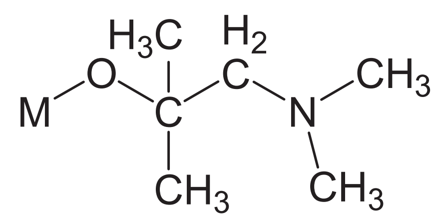
O^sBu = *sec*-butoxy 

O^tBu = *tert*-butoxy 

O^tPe = *tert*-pentoxy 

mmp = 1-methoxy-2-methyl-2-propoxy 

dmae = dimethylamino-ethoxy 

dmamp = 1-dimethylamino-2-methyl-2-propoxy 

Alkoxide Compounds Used in ALD

$Al(OEt)_3$ = tris(ethoxy)aluminum = aluminum ethoxide
$AlMe_2(O^iPr)$ = isopropoxydimethylaluminum
$B(OMe)_3$ = tris(methoxy)boron = trimethylborate
$Hf(O^tBu)_4$ = tetra(*tert*-butoxy)hafnium = hafnium *tert*-butoxide
$Hf(mmp)_4$ = tetra(1-methoxy-2-methyl-2-propoxy)hafnium
$Nb(OEt)_5$ = penta(ethoxy)niobium = niobium ethoxide
$Ni(dmamp)_2$ = bis(1-dimethylamino-2-methyl-2-propoxy)nickel(II)
$Pb(O^tBu)_2$ = bis(*tert*-butoxy)lead(II) = lead(II) *tert*-butoxide
$Si(OEt)_4$ = tetra(ethoxy)silane = tetraethylorthosilicate = TEOS
$Si(O^tBu)_3OH$ = tris(*tert*-butoxy)silanol
$Si(O^tPe)_3OH$ = tris(*tert*-pentoxy)silanol
$Ta(OEt)_5$ = penta(ethoxy)tantalum = tantalum ethoxide
$Ti(OMe)_4$ = tetra(methoxy)titanium = titanium methoxide
$Ti(OEt)_4$ = tetra(ethoxy)titanium = titanium ethoxide
$Ti(O^iPr)_4$ = tetra(isopropoxy)titanium = titanium isopropoxide
$VO(O^iPr)_3$ = tris(isopropoxy)oxovanadium = vanadyl isopropoxide

Elements with Alkoxide ALD Precursors

1																	18
H	2											13	14	15	16	17	He
Li	Be											**B**	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	**Al**	**Si**	P	S	Cl	Ar
K	Ca	Sc	**Ti**	**V**	Cr	Mn	Fe	Co	**Ni**	Cu	Zn	Ga	**Ge**	As	Se	Br	Kr
Rb	Sr	Y	**Zr**	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	**Hf**	**Ta**	W	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			Ce	Pr	Nd	Pm	Sm	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No	

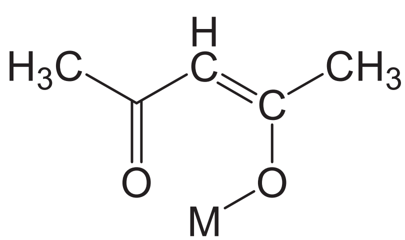
Advantages:
reactive to water vapor => oxides

Disadvantages:
limited thermal stability
not suitable for making nitrides
not suitable for making pure metals

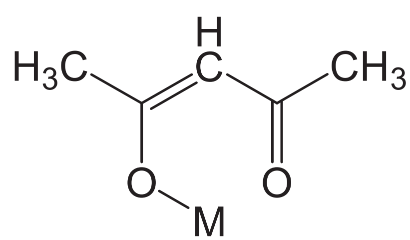
Beta-diketonate Compounds

4 equivalent ways to represent a metal acetylacetonate (acac):

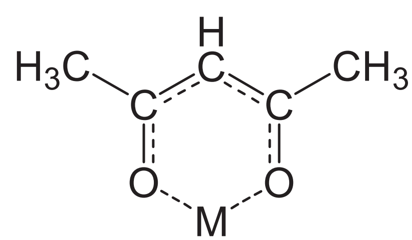
localized bonding picture 1



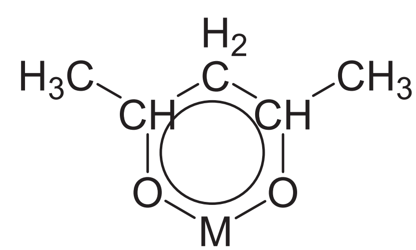
localized bonding picture 2



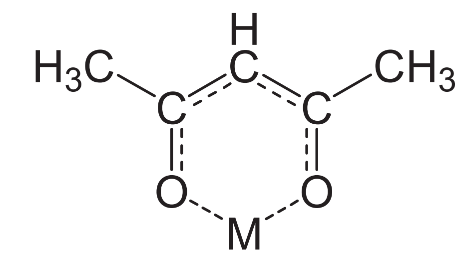
delocalized bonding picture 1



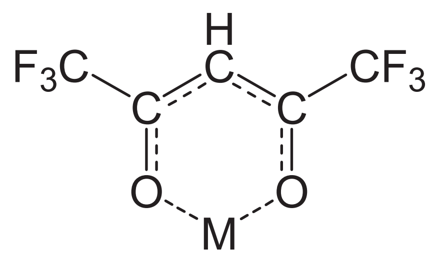
delocalized bonding picture 2



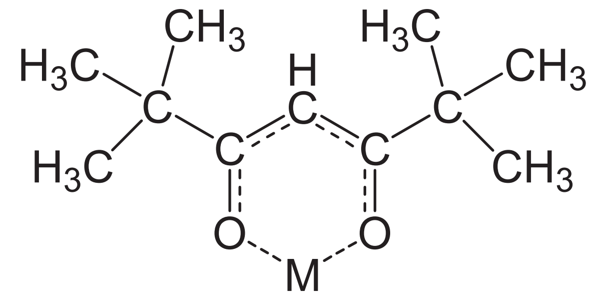
Beta-diketonate Compounds



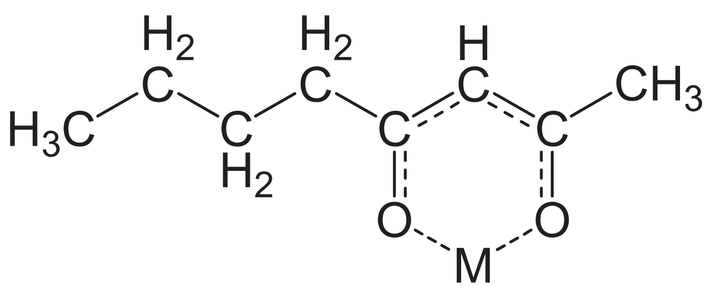
pentane-2,4-dionate, or
acetylacetonate (acac)



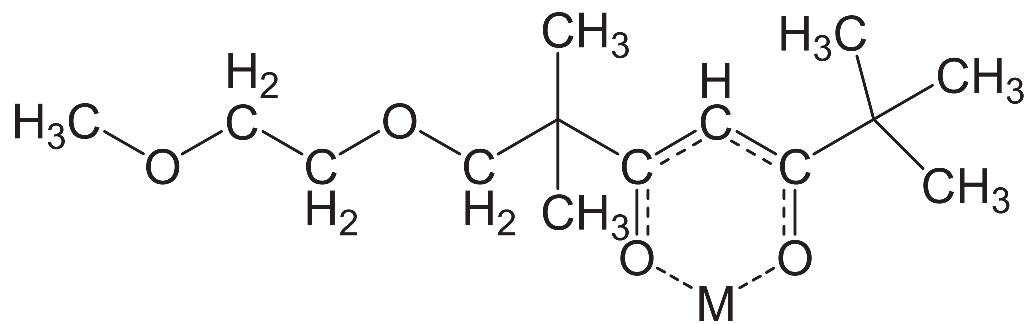
1,1,1,5,5,5-hexafluoro-
acetylacetonate (hfac)
(more volatile)



2,2,6,6-tetramethyl-
heptane-3,5-dionate
(thd or tmhd)
(more bulky)



octane-2,4-dionate (od)
(lower melting point)



1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-
heptane-3,5-dionate (methd)
(very bulky)

Beta-diketonate ALD Precursors

$Ba(thd)_2$
$Ce(thd)_4$
$Co(acac)_2$
$Co(acac)_3$
$Co(thd)_3$
$Cr(acac)_3$
$Cu(hfac)_2$
$Cu(thd)_2$
$Dy(thd)_3$
$Er(thd)_3$
$Eu(thd)_3$
$Fe(acac)_3$
$Fe(thd)_3$
$Gd(thd)_3$
$Ho(thd)_3$
$Ir(acac)_3$
$La(thd)_3$
$Mg(thd)_2$
$Mn(thd)_3$
$Nd(thd)_3$
$Ni(acac)_2$
$Ni(thd)_2$
$Pb(thd)_2$
$Pd(hfac)_2$
$Pd(thd)_2$
$Pt(acac)_2$
$Ru(thd)_3$
$Ru(od)_3$
$Sc(thd)_3$
$Sm(thd)_3$
$Sr(thd)_2$
$Sr(methd)_2$
$Tm(thd)_3$
$Y(thd)_3$

Advantages:

non-reactive to ambient air
high thermal stability

Disadvantages:

low vapor pressure (except $Cu(hfac)_2$)
solids with high melting points
low reactivity to water vapor
not suitable for making nitrides

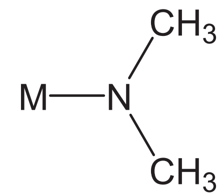
Beta-diketonate ALD Precursors

1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	**Mg**	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	Zn	**Ga**	Ge	As	Se	Br	Kr
Rb	**Sr**	**Y**	**Zr**	Nb	Mo	Tc	**Ru**	**Rh**	**Pd**	Ag	Cd	**In**	Sn	Sb	Te	I	Xe
Cs	**Ba**	**La**	**Hf**	Ta	W	**Re**	**Os**	**Ir**	**Pt**	Au	Hg	Tl	**Pb**	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

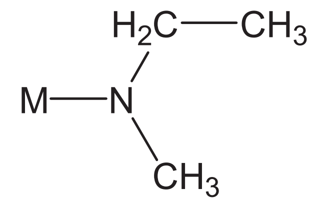
Ce	Pr	**Nd**	Pm	**Sm**	**Eu**	**Gd**	Tb	**Dy**	**Ho**	**Er**	**Tm**	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Amide Ligands

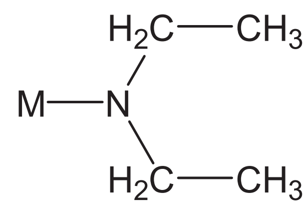
NMe_2 = dimethylamino = dimethylamido



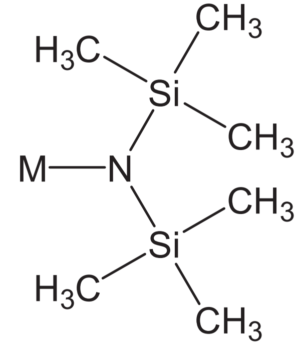
NEtMe = ethylmethylamino = ethylmethylamido



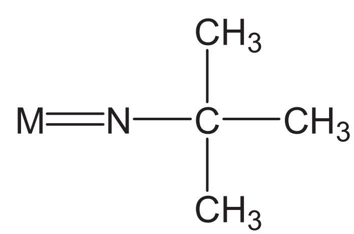
NEt_2 = diethylamino = diethylamido



$N(SiMe_3)_2$ = bis(trimethylsilyl)amido = bis(trimethylsilyl)amino



N^tBu = tert-butylimino = tert-butylimido



Amide and Imide Precursors for ALD

$Al(NMe_2)_3$ = tris(dimethylamido)aluminum
= $Al_2(NMe_2)_6$ = hexakis(dimethylamido)dialuminum
$Bi[N(SiMe_3)_2]_3$ = tris(bis(trimethylsilyl)amido)bismuth
$Hf(NMe_2)_4$ = tetrakis(dimethylamido)hafnium
$Hf(NEtMe)_4$ = tetra(ethylmethylamido)hafnium = TEMAH
$Hf(NEt_2)_4$ = tetrakis(diethylamido)hafnium = TDEAH
$La[N(SiMe_3)_2]_3$ = tris(bis(trimethylsilyl)amido)lanthanum
$Pr[N(SiMe_3)_2]_3$ = tris(bis(trimethylsilyl)amido)praseodymium
$Ta(NMe_2)_5$ = pentakis(dimethylamido)tantalum
$Ta(NEt_2)_5$ = pentakis(diethylamido)tantalum
$Ta(NtBu)(NEt_2)_3$ = (*tert*-butylimido)tris(diethylamido)tantalum
$Ti(NMe_2)_4$ = tetrakis(dimethylamido)titanium
$Ti(NEtMe)_4$ = tetra(ethylmethylamido)titanium = TEMAT
$W(NtBu)_2(NMe_2)_2$ = bis(tert-butylimido)bis(dimethylamido)tungsten
$Zn[N(SiMe_3)_2]_2$ = bis(bis(trimethylsilyl)amido)zinc
$Zr(NMe2)_4$ = tetrakis(dimethylamido)zirconium
$Zr(NEtMe)_4$ = tetra(ethylmethylamido)zirconium = TEMAZ
$Zr(NEt_2)_4$ = tetrakis(diethylamido)zirconium = TDEAZ

Amide and Imide Precursors for ALD

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	**Be**											B	C	N	O	F	Ne
Na	Mg											**Al**	**Si**	P	S	Cl	Ar
K	Ca	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	Br	Kr
Rb	Sr	**Y**	**Zr**	**Nb**	**Mo**	Tc	Ru	Rh	Pd	Ag	Cd	In	**Sn**	**Sb**	**Te**	I	Xe
Cs	Ba	**La**	**Hf**	**Ta**	**W**	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	**Bi**	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ce	**Pr**	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

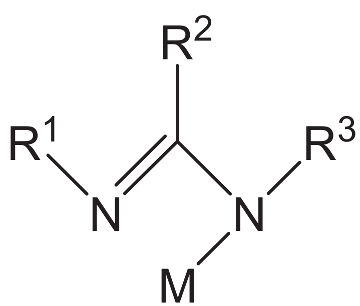
Advantages:
highly reactive
suitable for oxides and nitrides

Disadvantages:
limited thermal stability
silicon impurity from silylamides

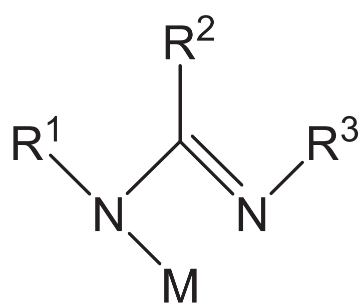
Amidinate Compounds

4 equivalent ways to represent a metal amidinate:

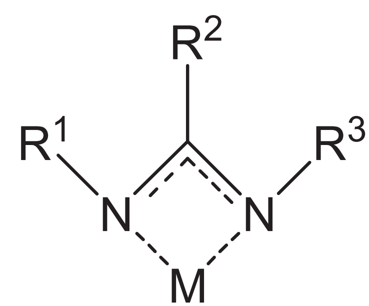
localized bonding picture 1



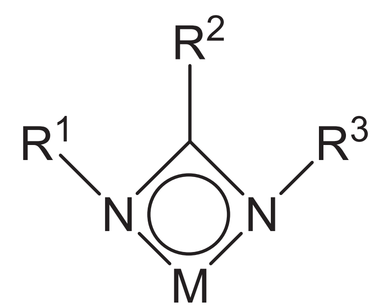
localized bonding picture 2



delocalized bonding picture 1

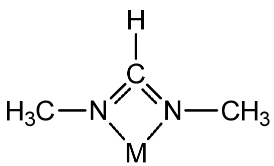


delocalized bonding picture 2

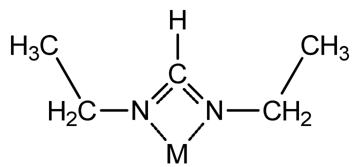


R^1, R^2 and R^3 are non-metals, usually alkyl groups C_xH_{2x+1}; other non-metals, such as silicon or nitrogen may be included.

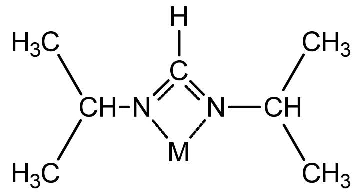
Some Amidinate Ligands



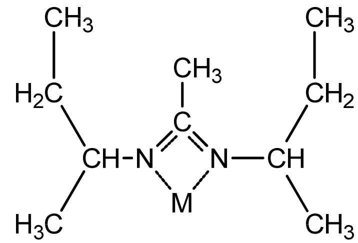
N,N’-dimethyl-formamidinate (Me_2fmd)



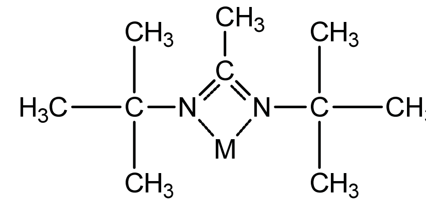
N,N’-diethyl-formamidinate (Et_2fmd)



N,N’-diisopropyl-formamidinate ($^iPr_2$fmd)

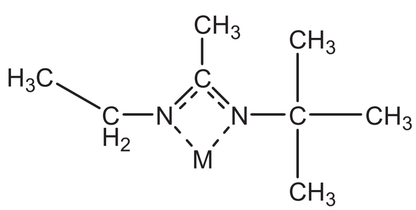


N,N’-di-*sec*-butyl-acetamidinate ($^sBu_2$amd)

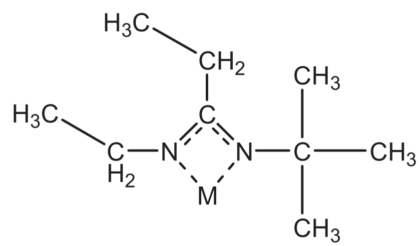


N,N’-dimethyl-acetamidinate ($^tBu_2$amd)

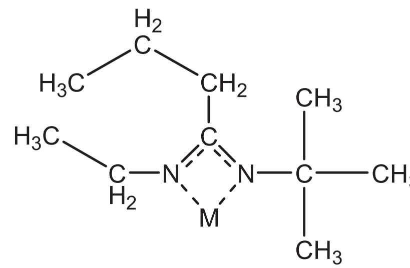
Increasing steric bulk →



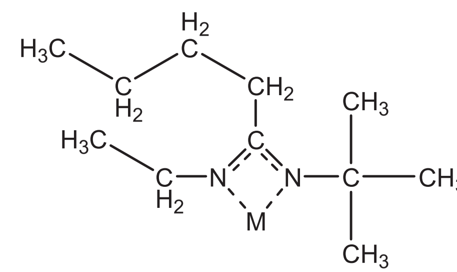
N’-*tert*-butyl-N-ethyl-acetamidinate (^{t}BuEt-amd)



N’-*tert*-butyl-N-ethyl-propionamidinate (^{t}BuEt-pmd)



N’-*tert*-butyl-N-ethyl-butyramidinate (^{t}BuEt-bmd)



N-ethyl-N’-*tert*-butyl-pentylamidinate (^{t}BuEt-pemd)

Increasing flexibility leads to decreasing melting points and liquids →

Amidinate Compounds Used in ALD

$Ag_2(^tBu_2\text{-amd})_2$
$Ca(^tBu_2\text{-amd})_2$
$Co(^iPr_2\text{-amd})_2$
$Co(^tBuEt\text{-amd})_2$
$Cr(Et_2\text{-amd})_3$
$Cu_2(^iPr_2\text{-amd})_2$
$Cu_2(^sBu_2\text{-amd})_2$
$Er(^tBu_2\text{-amd})_3$
$Fe(^iPr_2\text{-amd})_2$
$Fe(^tBuEt\text{-amd})_2$
$Ga(Et_2\text{-amd})_3$
$Gd(^iPr_2\text{-amd})_3$
$Hf(Me_2\text{-fmd})_4$
$Hf(Me_2\text{-pmd})_4$
$Hf(Me_2\text{-bmd})_4$
$La(^iPr_2\text{-fmd})_3$
$La(^tBu_2\text{fmd})_3$

$Lu(Et_2\text{-fmd})_3$
$Lu(Et_2\text{-amd})_3$
$Mg(^tBu_2\text{amd})_2$
$Mg(^iPr_2\text{-amd})_2$
$Mn(^tBu_2\text{-pemd})_2$
$Ni(^tBu_2\text{-amd})_2$
$Pr(^iPr_2\text{-amd})_3$
$Sc(Et_2\text{-amd})_3$
$Sr(^tBu_2\text{-amd})_2$
$Ti(^iPr_2\text{-amd})_3$
$V(Et_2\text{-amd})_3$
$V(^iPr_2\text{-amd})_3$
$Y(^iPr_2\text{-amd})_3$
$Zn(^iPr_2\text{-amd})_2$
$Zr(Me_2\text{-fmd})_4$
$Zr(Me_2\text{-pmd})_4$
$Zr(Me_2\text{-bmd})_4$

Advantages:

high reactivity to water => oxides
high reactivity to ammonia => nitrides
high reactivity to H_2S => sulfides
reactive to hydrogen gas H_2 => metals

Disadvantages:

several different ligands needed
some are solids, not liquids

Amidinate ALD Precursors

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	**Mg**											**Al**	Si	P	S	Cl	Ar
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	As	Se	Br	Kr
Rb	**Sr**	**Y**	**Zr**	Nb	Mo	Tc	**Ru**	Rh	Pd	**Ag**	Cd	**In**	**Sn**	Sb	Te	I	Xe
Cs	**Ba**	**La**	**Hf**	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	**Bi**	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ce	**Pr**	**Nd**	Pm	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Structures of Metal(II) Acetamidinates

Increasing ligand bulk →

tert-butyl$_2$	m	m	m	m	m	m	d	d	d
isopropyl$_2$	m	m	m	d	d	d	d	p	p
^{t}Bu-Et	m	d	d	d				p	p
n-propyl$_2$		d							
	Ni	Co	Cr	Fe	Mg	Mn	Ca	Sr	Ba

Increasing size of metal atom →

m = volatile monomer

d = volatile dimer

p = non-volatile polymer

Structures of Metal(III) Acetamidinates

Increasing ligand bulk →

tert-butyl$_2$					n				m	m		m	m		m	m	d
isopropyl$_2$	m		m	m	m	m	m	m		r	r			r		r	d
Et-^{t}Bu								r								d	
n-propyl$_2$		m		m			r	d		d						d	
Et$_2$							r	d									
	Al	Cr	Ga	V	Ti	Ru	Sc	Lu	Er	Y	Gd	Eu	Nd	Pr	Ce	La	Bi

Increasing size of metal atom →

n = non-existent?

m = more crowded, less reactive monomer, reacts with ozone, O_3

r = more reactive monomer, reacts with water, H_2O, & ammonia, NH_3

d = volatile dimer

d = low-volatility dimer

TYPES OF ALD REACTIONS

ALD reactions usually transfer one atom
from a surface-bound group to a vapor group, or
from a vapor group to a surface-bound group (the reverse direction).

The transferred atoms are usually hydrogen, oxygen, fluorine or chlorine.

A few reactions transfer a whole group of atoms, not just a single atom.

Examples of ALD Reactions

water H-transfer reactions => metal oxides

ozone O-transfer reactions => metal oxides

silanol H-transfer reactions => metal silicates

ammonia H-transfer reactions => metal nitrides

H-reduction reactions => transition metals

oxygen O-transfer reactions => noble metals (Pt, Ru, Ir)

fluoride to silicon reactions => tungsten or molybdenum

chloride to trialkylsilyl reactions => selenides or tellurides

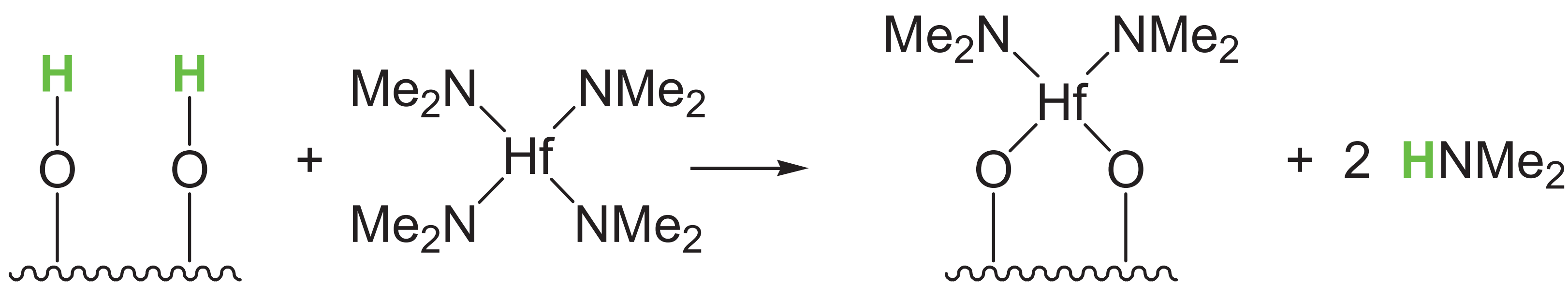
ethanolamine H-transfer reactions => incorporated organic groups

Oxides by Hydroxyl Exchange & Hydrolysis

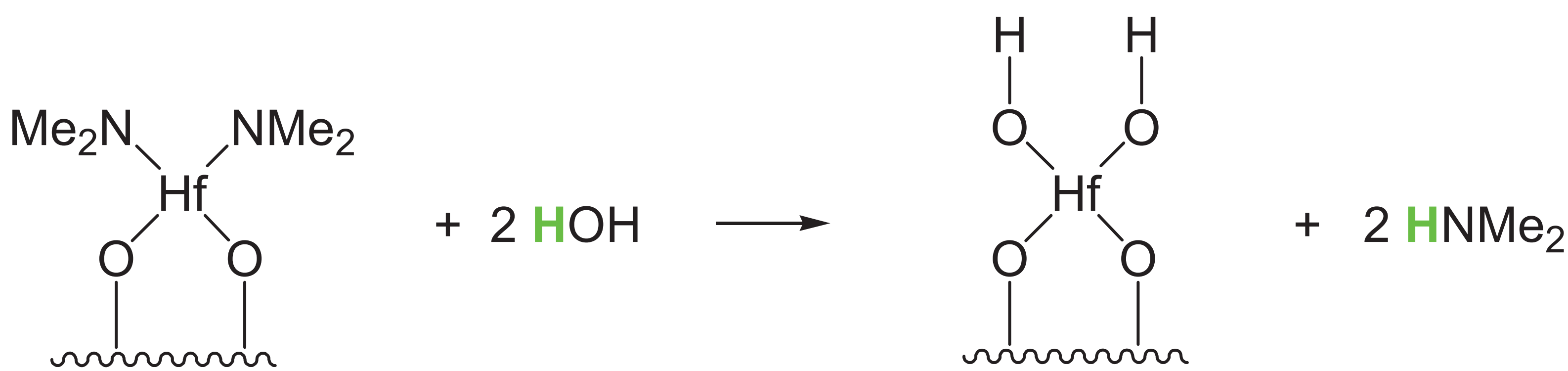
Tetrakis(dimethylamido)hafnium reacts with water to make hafnium dioxide

$$Hf(NMe_2)_4 + 2\,H_2O \Rightarrow HfO_2 + 4\,HNMe_2$$

Chemisorption by hydrogen transfer to ligands to form dimethylamine gas:



Transfer of hydrogen from water to surface-bound dimethylamide ligands:

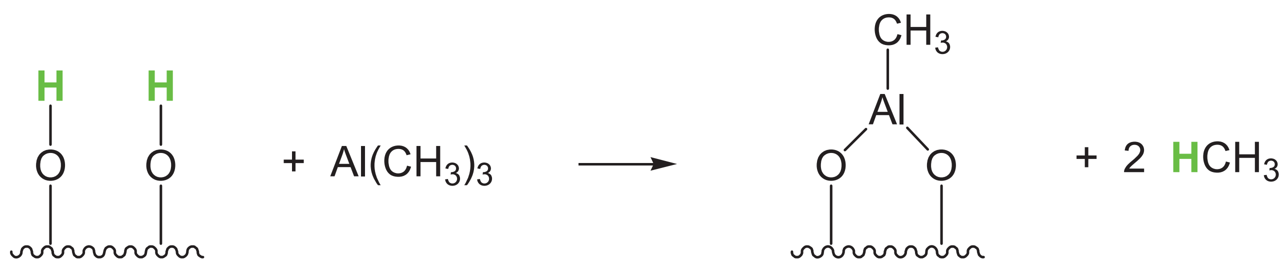


Oxides by Oxidation with Ozone

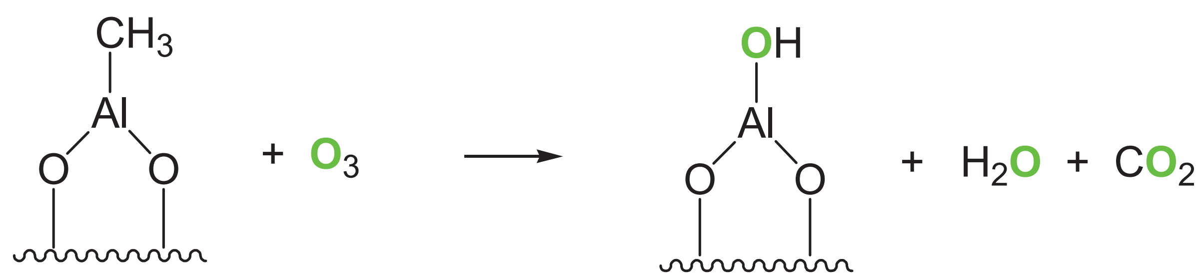
Trimethylaluminum reacts with ozone to make aluminum oxide:

$$(CH_3)_3Al + O_3 \Rightarrow Al_2O_3 + CH_4 + H_2O + CO_2$$

Hydrogen atom transfer from surface hydroxyl to ligand to form methane:



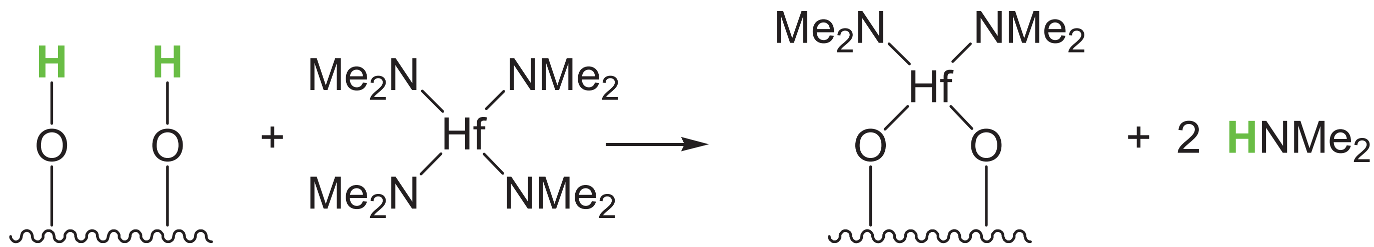
Oxygen atom transfer to surface ligand to form water and carbon dioxide:



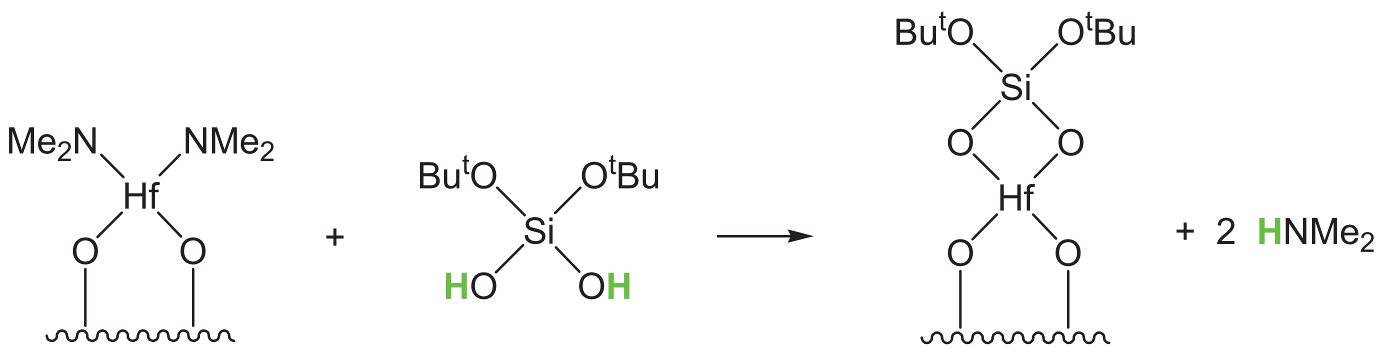
Water may not be detected because it reacts with other surface CH_3 groups

Metal Silicates from Silanol

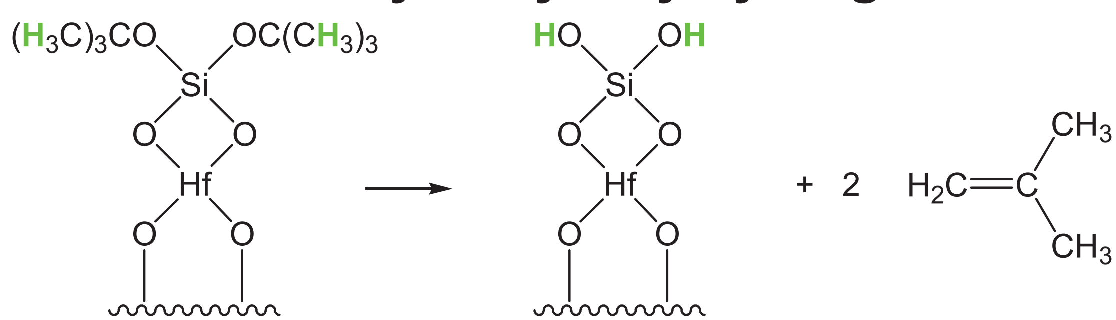
Hydrogen atom transfer from surface hydroxyls to dimethylamide ligands:



Hydrogen atom transfer from silanol to surface-bound dimethylamides:



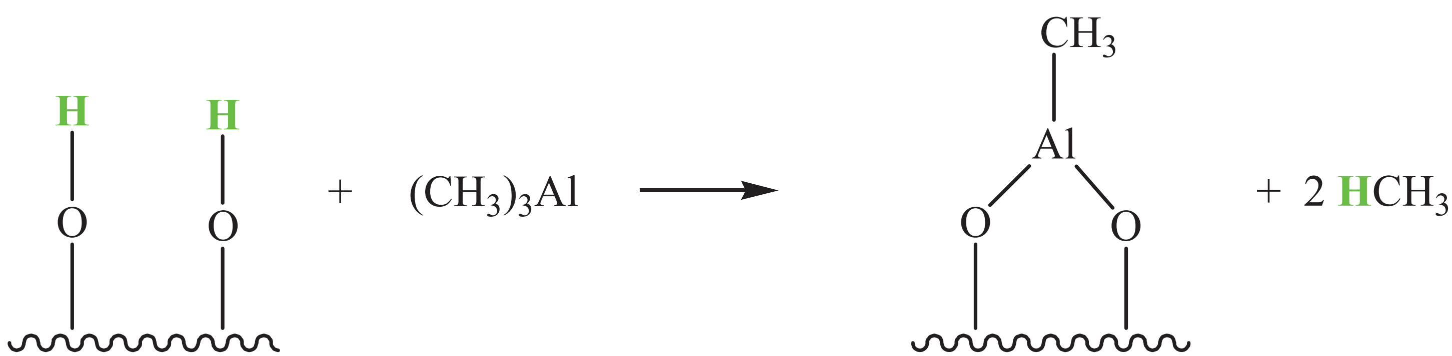
Regeneration of surface hydroxyls by hydrogen from tertiary butyl groups:



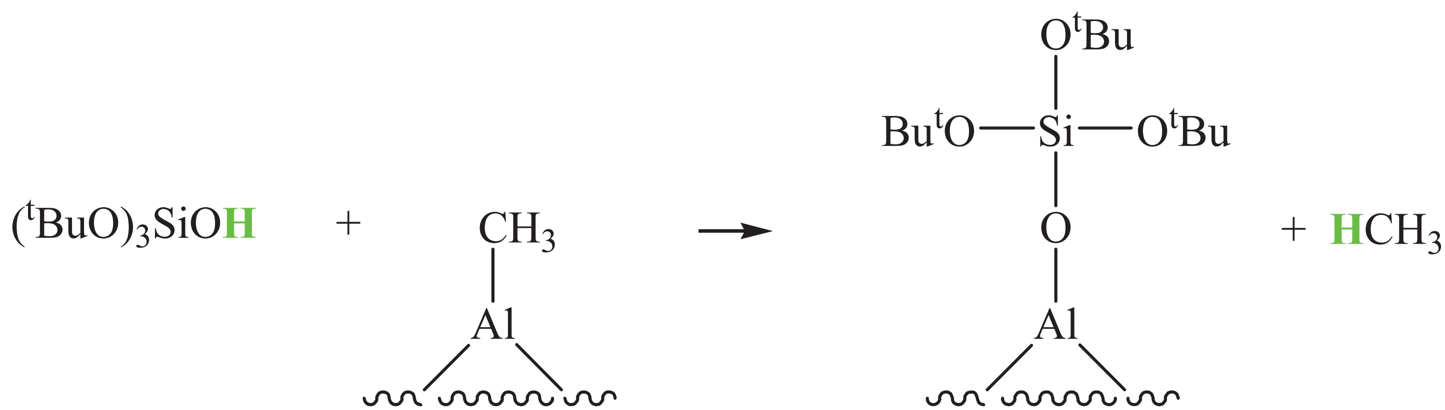
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

=> very large growth per cycle, up to 15 nm, > 50 monolayers

Hydrogen atom transfer from surface hydroxyl to methyl ligands:

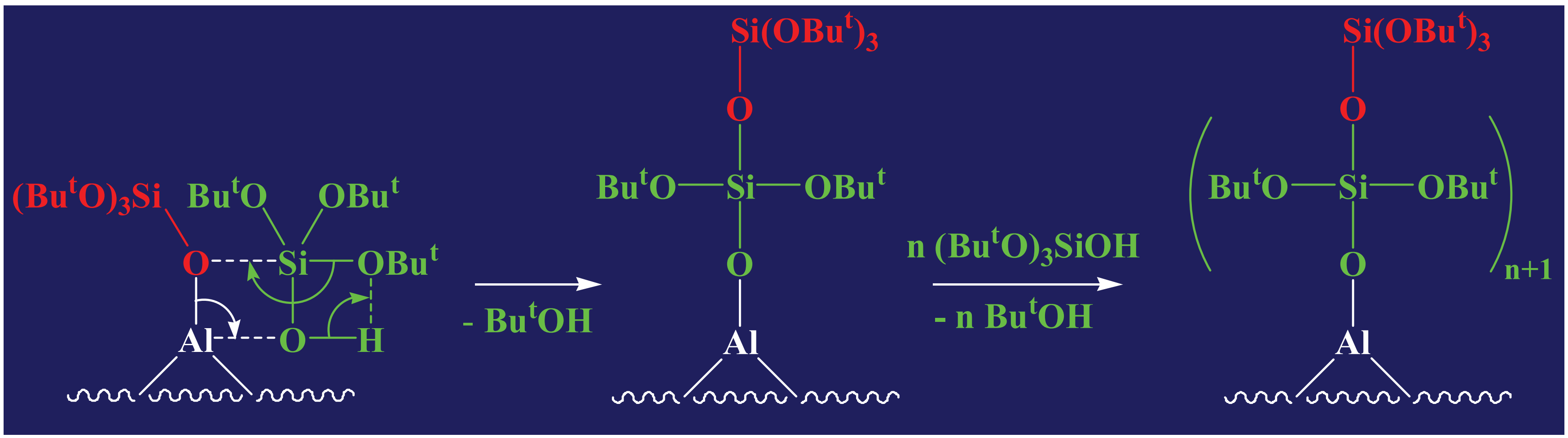


Hydrogen atom transfer from silanols to methyl ligands:



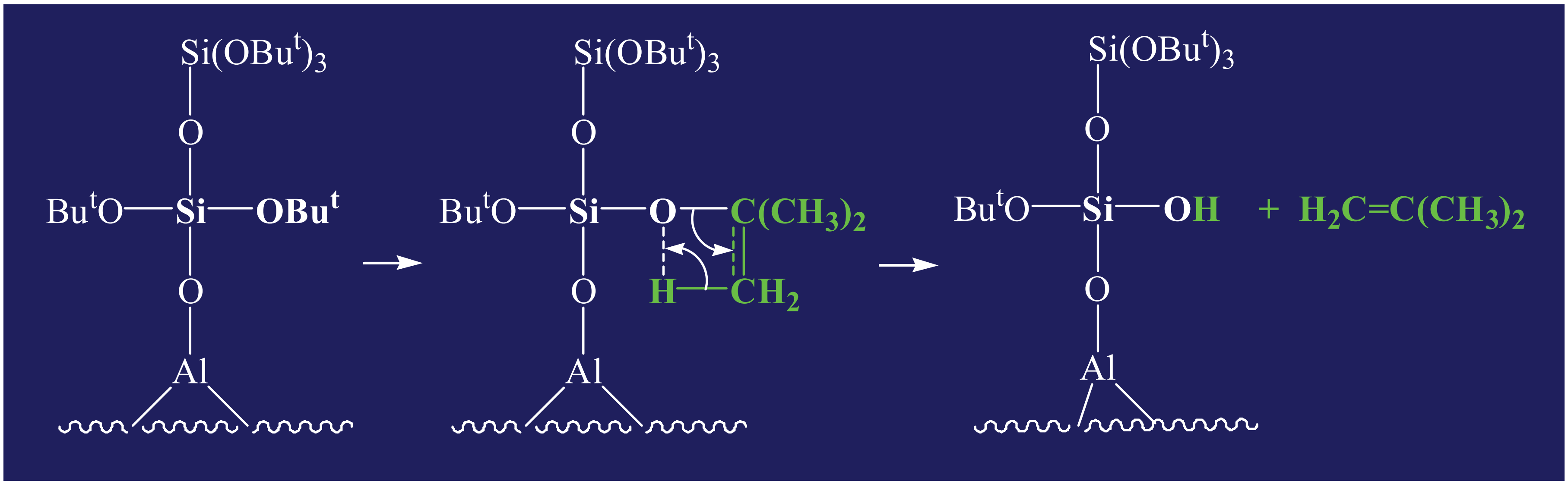
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

Repeated insertions of $(^tBuO)_3SiOH$ into an Al-O bond produces a siloxane polymer tethered to the surface:



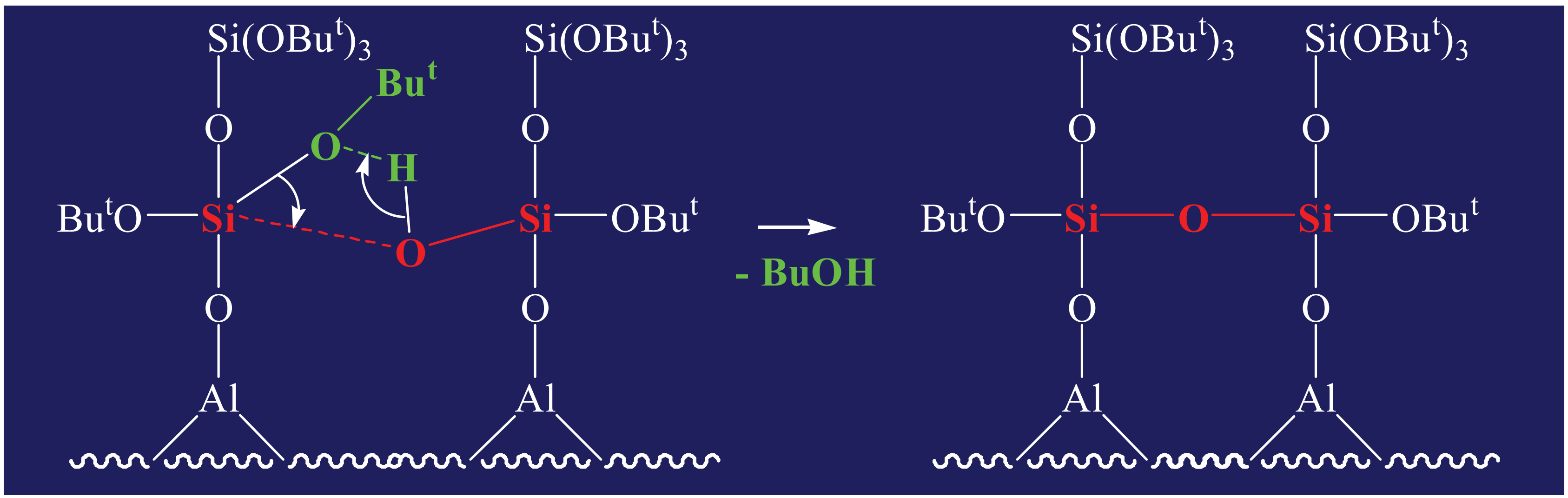
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

Elimination of isobutene by β-hydrogen transfer:



Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

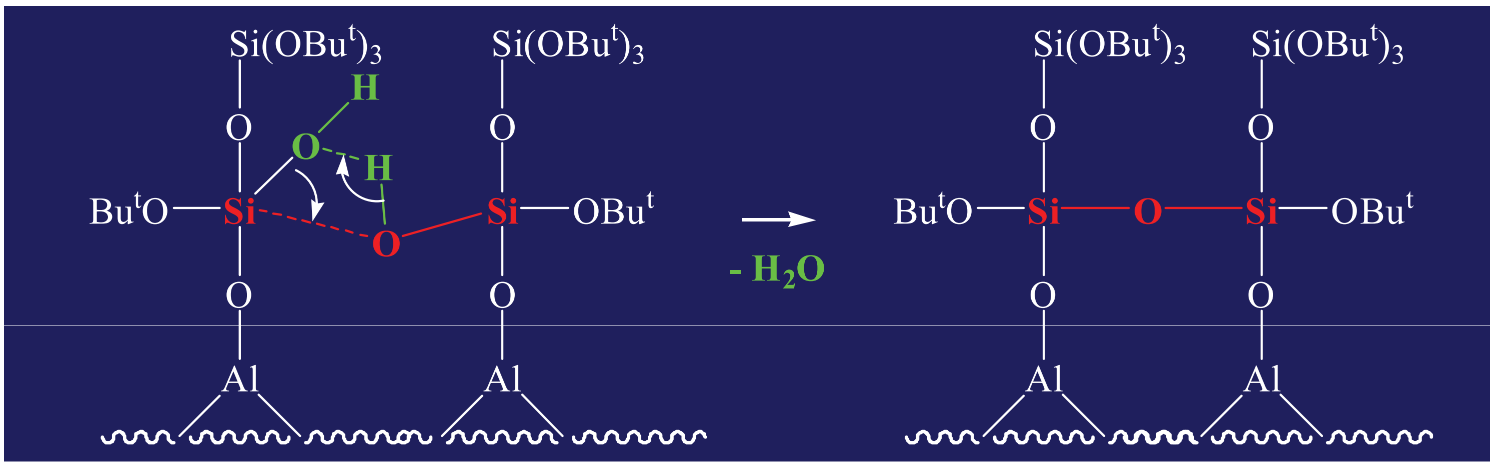
Siloxane polymer chains cross-link by elimination of *tert*-butanol:



Complete crosslinking produces a solid silica layer that is impervious to diffusion of more silanol up to the aluminum catalyst, so reaction stops.

Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

Elimination of water also cross-links polymer chains:



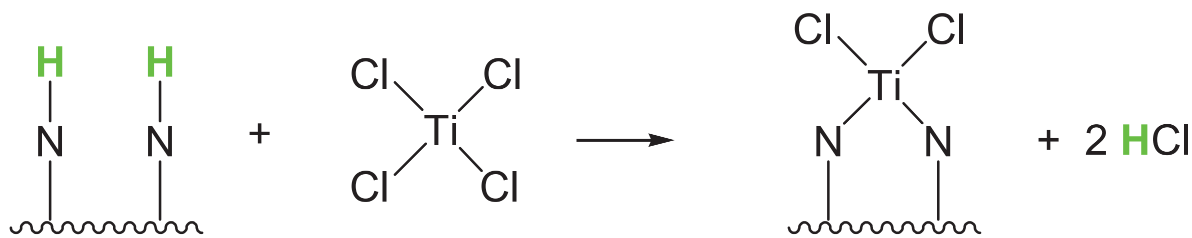
Complete crosslinking produces a solid silica layer that is impervious to diffusion of more silanol up to the aluminum catalyst, so reaction stops.

Nitrides by Chloride Exchange and Reduction

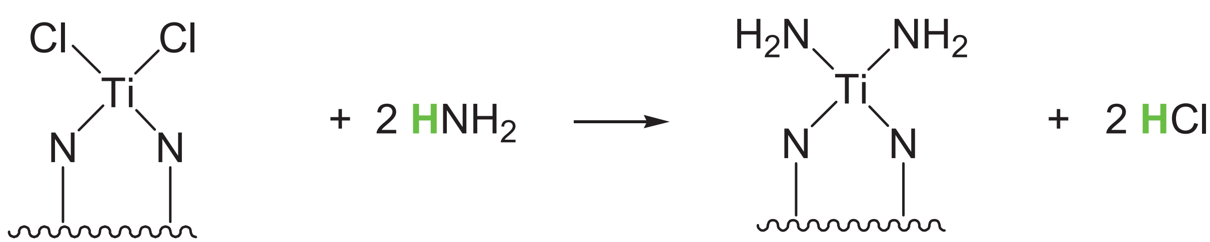
Titanium(IV) tetrachloride plus ammonia makes titanium(III) nitride:

$$\mathbf{TiCl_4 + NH_3 \Rightarrow TiN}$$

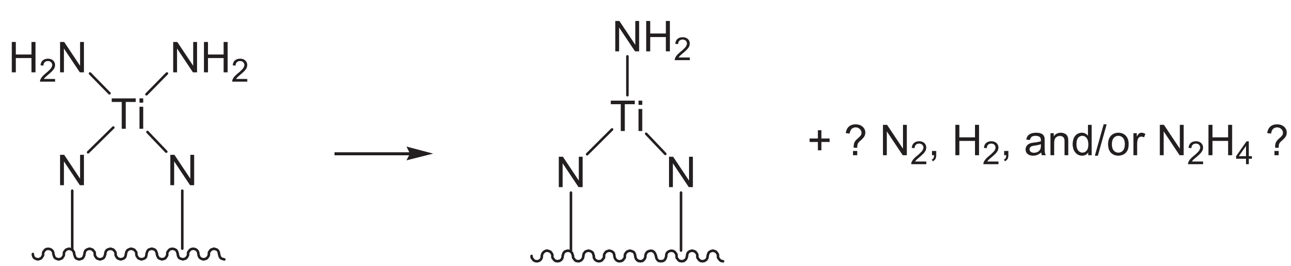
Hydrogen atom transfer from surface amides to chlorides on precursor:



Hydrogen atom transfer from ammonia to surface-bound chloride ligands:

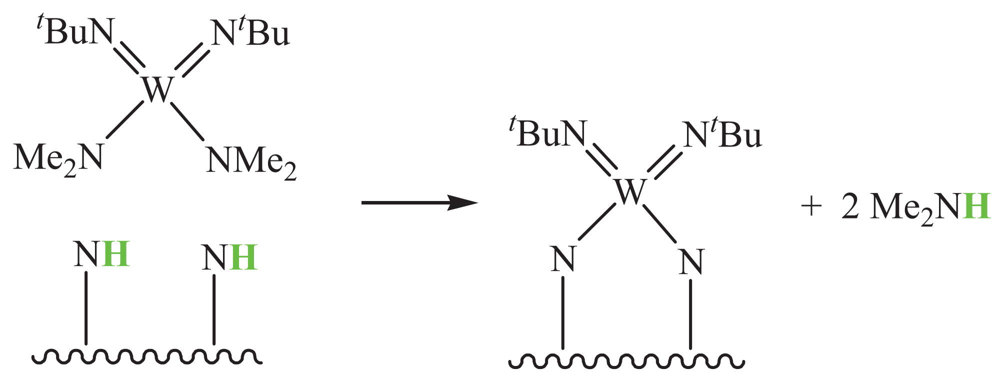


Titanium in oxidation state +4 is reduced to +3 by elimination reactions:

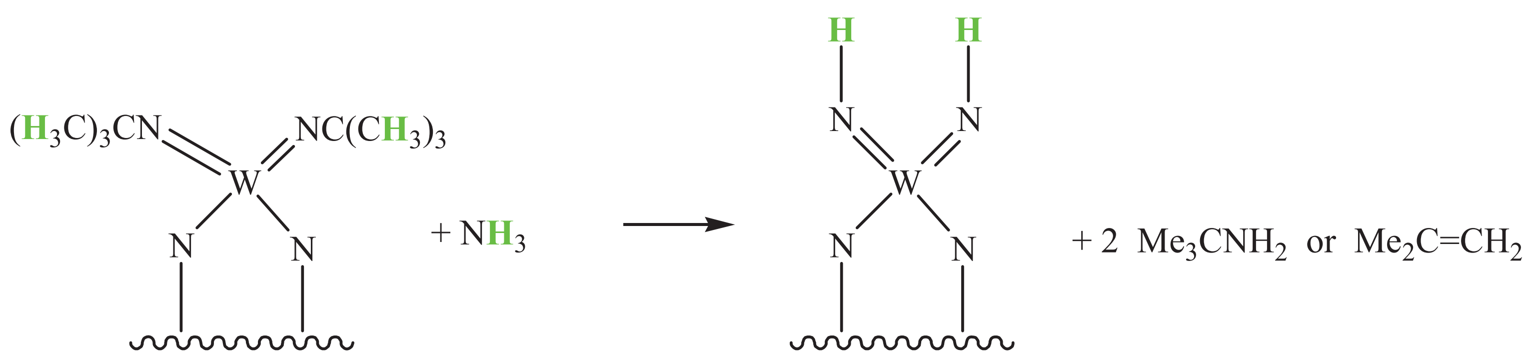


Tungsten Nitride by Exchange and Catalysis

Hydrogen transfer from surface imides to dimethylamides on precursor:



Hydrogen transfer to imides from ammonia or from *tert*-butyl imido group?



Reductive elimination of nitrogen to reduce W(VI) to W(III)

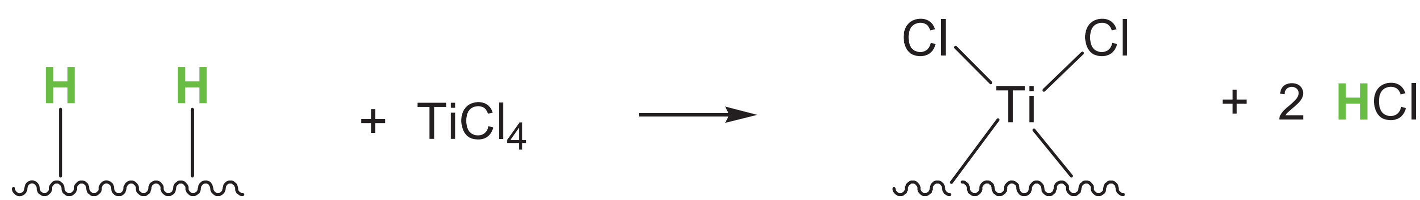
$$\mathbf{WN_2 \;\Rightarrow\; WN + \tfrac{1}{2} N_2}$$

Metals by Reduction with H Atoms

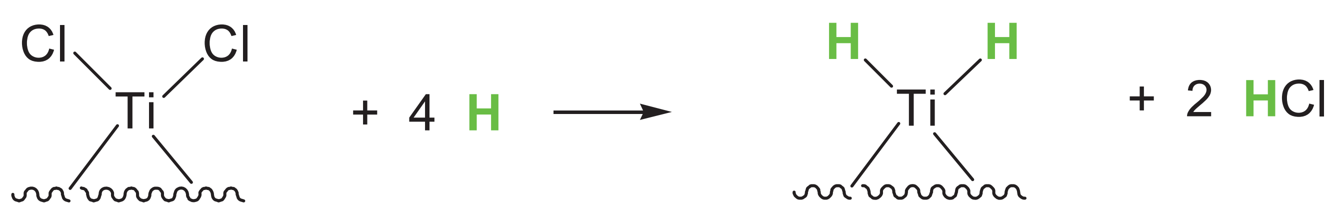
Titanium from titanium tetrachloride and hydrogen atoms in a plasma

$$TiCl_4 + 4\,H \Rightarrow Ti + 4\,HCl$$

Hydrogen atoms on surface transfer to chlorides on precursor:

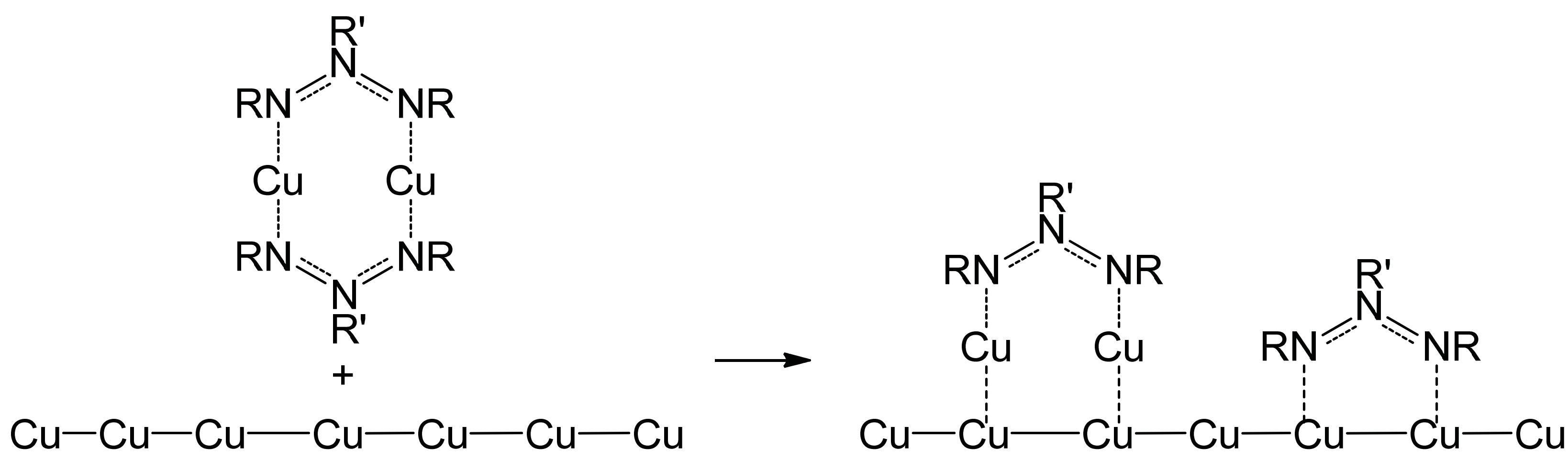


Hydrogen atoms from plasma remove chlorine as hydrogen chloride gas:

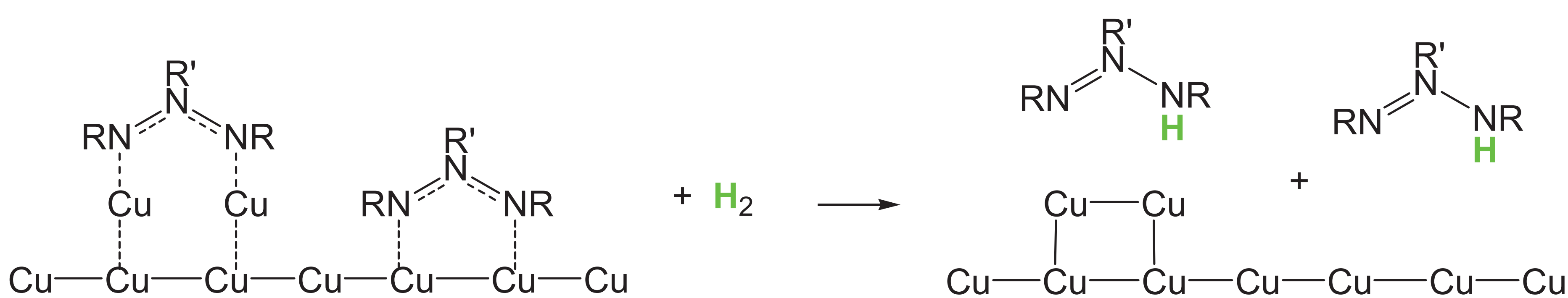


Metals by Reduction with H_2 Molecules

Dissociative chemisorption of copper amidinate on a copper surface:

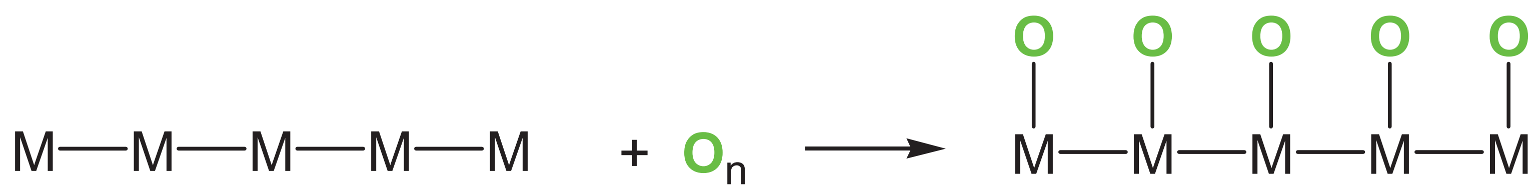


Hydrogen transfer to amidinate ligands to make copper & amidine vapor:

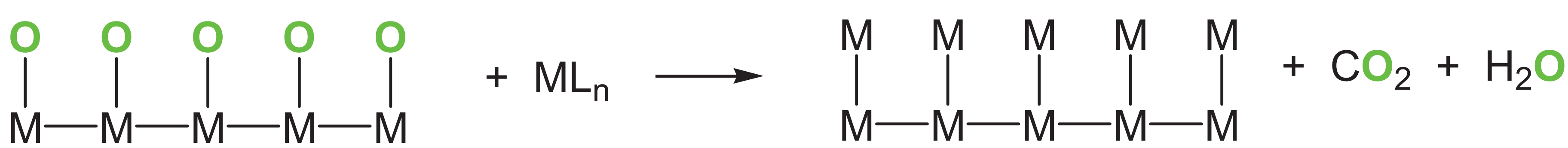


Noble Metals by Oxidation Reactions

Oxygen atoms chemisorb on noble metals (platinum, ruthenium, etc.):



Adsorbed oxygen atoms burn ligands to form carbon dioxide and water:



Tungsten Metal by Fluoride Exchange

Overall reaction: $WF_6 + Si_2H_6 \Rightarrow W + 2\ SiF_3H + 2\ H_2$

a F atom moves from WF_6 vapor to liberate Si from surface:

$$\text{surface-}WSiF_2H + WFF_5 \Rightarrow \text{surface-}WWF_5 + SiFF_2H$$

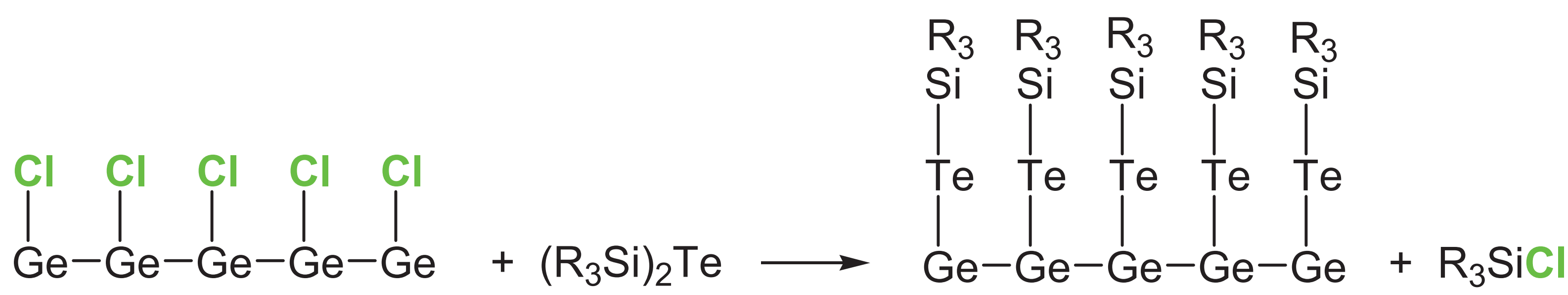
3 F atoms move from W on surface to break up Si_2H_6 vapor:

$$\text{surface-}WWF_2F_3 + Si_2H_6 \Rightarrow \text{surface-}WWSiF_2H + SiF_3H + 2\ H_2$$

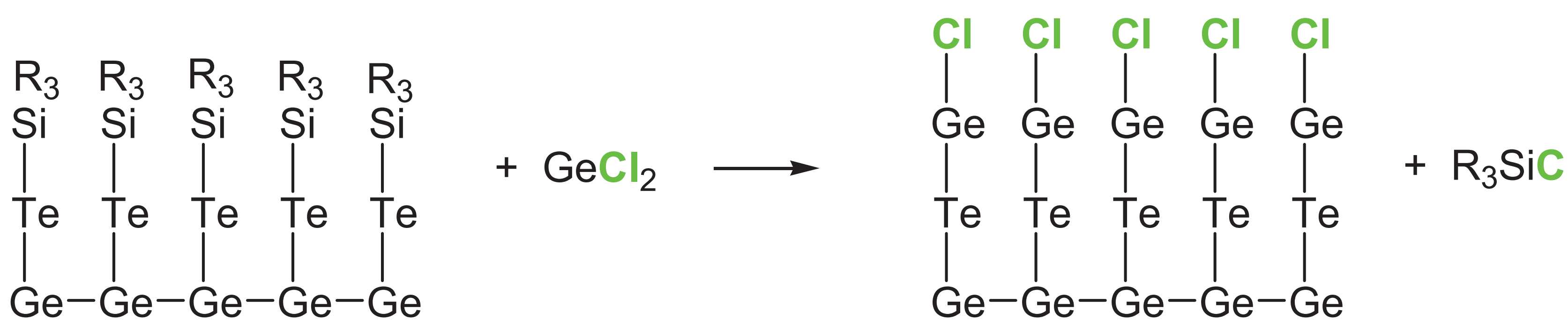
A very complex reaction, breaking 1 Si-Si, 5 W-F and 4 Si-H bonds while forming a new W-Si bond, 5 new Si-F bonds and 2 new H-H bonds

Tellurides by Chloride Exchange Reactions

Chlorine atoms on surface move to trialkylsilyl groups on tellurium:



Chlorine atoms on germanium remove surface trialkylsilyl groups:



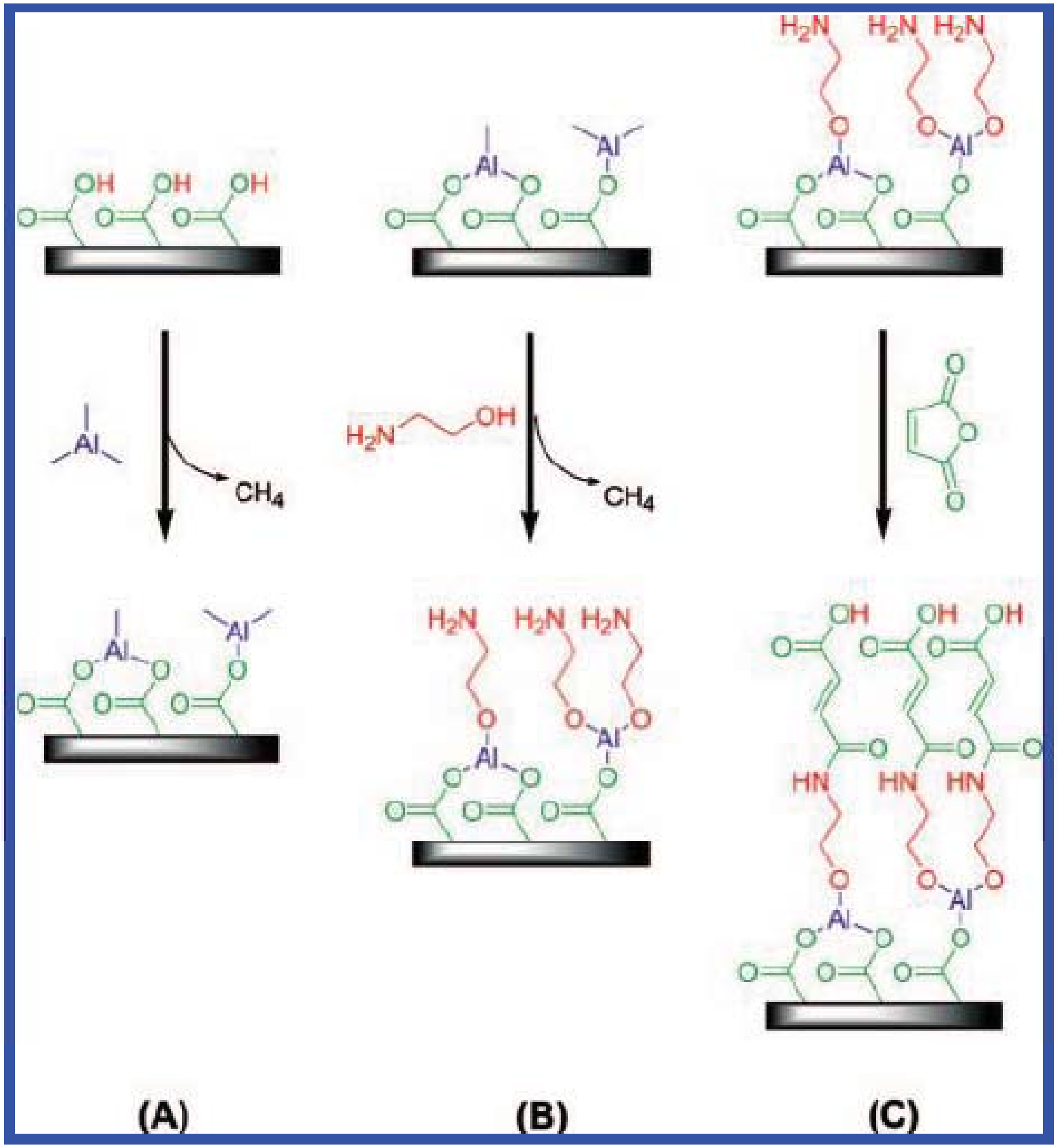
Adding Organic Components to ALD Films

A) trimethylaluminum

B) ethanolamine

C) maleic anhydride

Adds flexibility to brittle inorganic films



from S. M. George, *Chem. Rev.* **110**, 111 (2010)

Problems When the Chemistry is Wrong

Thermal decomposition

- **destroys the self-limiting property of surface reactions**
- **thickness uniformity, step coverage and film purity degraded**

Incomplete surface reactions can incorporate ligands as impurities

- **slow kinetics can be alleviated by longer exposure times, or**
- **too low thermodynamic driving force => change precursors**

Incomplete step coverage

- **need longer exposure time or higher precursor vapor pressure**
- **but may be limited by decomposition or desorption of precursor**

Etching by precursor or reaction byproducts

- **mostly from halide precursors (chlorides, bromides)**

Summary

ALD precursors are available for most non-radioactive elements

Suitable reactant pairs are known for ALD of

- **some pure elements**
- **oxides of most elements**
- **nitrides of many elements**
- **sulfides, selenides and tellurides of some elements**
- **phosphides and arsenides of a few elements**
- **fluorides of a few elements**

ALD reactions usually involve

- **exchange reactions between surface groups and vapor groups**
- **exchanged atoms are usually hydrogen, oxygen or halogen**

Summary

Recent Reviews of ALD Chemistry

R. Puurunen, *J. Appl. Phys.* 97, 121301 (2005)

J. Paivasaari et al., *Topics in Appl. Phys.* 106, 15 (2007)

M. Ritala and J. Niinisto, in *Chemical Vapor Deposition* (Royal Society of Chemistry, 2009)

S. M. George, *Chem. Rev.* 110, 111 (2010)

S. D. Elliott, *Langmuir* 26, 9179 (2010)

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Yiqun Liu
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